

PATENT SPECIFICATION

(11) 1 602 777

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- (21) Application No. 23420/78 (22) Filed 26 May 1978
 (31) Convention Application No. 825327
 (32) Filed 17 Aug. 1977 in
 (33) United States of America (US)
 (44) Complete Specification published 18 Nov. 1981
 (51) INT CL³ B01J 21/12 29/08
 (52) Index at acceptance

CIA 13 N34 N4 PB1

BIE 1111 1121 1125 1128 1197 1203 1212 1242 1285 1298 1302
 1322 1363 1381 1500 1518 1519 1611 1631 1632 1633
 1634 1635 1702 1705 1714 1715 1724 1725 1739 1741
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(54) A NOVEL HYDROSOL AND CRACKING CATALYST PREPARED FROM IT

(71) We, W. R. GRACE & CO., a corporation organized and existing under the laws of the State of Connecticut, United States of America, of Grace Plaza, 114 Avenue of the Americas, New York 10036, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:

This invention relates to a silica sol which may be gelled to form a matrix for a cracking catalyst consisting of zeolites in a matrix containing silica gel.

A well known type of catalyst for cracking hydrocarbons is silica gel, formed by gelation of a silica hydrosol, which can be the matrix of a composite catalyst containing also zeolites or clay. U.S. Patent No. 3,867,308 describes a process for preparing a hydrocarbon cracking catalyst by preparing a hydrosol by rapid addition of mineral acid to sodium silicate, adjusting the pH of the hydrosol, adding clay and zeolite components, spary drying, washing with water, rare earth exchanging and recovering the product.

U.S. Patent 3,957,689 discloses an improvement in such a composite namely catalysts comprising clay or zeolite, together with a gel formed from silica-alumina hydrosol in place of silica hydrosol.

Another improvement on silica hydrosol for such catalysts is disclosed in U.S. Patent No. 4,022,714. According to that patent a sodium silicate solution is acidified to make silica hydrosol and the precursor of an oxide of a metal is added to the hydrosol. The modified hydrosol with clay incorporated in it, is mixed with a slurry of zeolites and the mixture is spray dried. In a preferred case, the metal whose oxide precursor is added to the silica hydrosol is titanium, so there is formed a catalyst containing silica-titania gel.

We have now found that the silica-titania hydrosol disclosed in U.S. Patent No. 4,022,714 can be improved so as to give a catalyst which is more uniform and has greater attrition resistance. This is achieved, according to the present invention, by incorporating alumina in the silica-titania hydrosol. Thus the present invention provides a hydrosol suitable for preparation of a hydrocarbon cracking catalyst which is a silica-titania-alumina hydrosol as defined below. This hydrosol can be dried to give a silica-alumina-titania dried product. There is also provided, according to our invention, a method of making a hydrocarbon conversion catalyst which comprises spray drying a slurry containing a zeolite and a titania-alumina-silica hydrosol.

The hydrosol of this invention can also be used as binder for a cracking catalyst containing clay instead of or in addition to the zeolite.

More specifically, we have found that a titania-alumina-silica hydrosol which is particularly useful for the preparation of bound clay/zeolite catalyst compositions may be prepared by combining mixed acid salt solutions of titanium and aluminium with alkali metal silicate solutions to form hydrosols having a pH of from 2.5 to 3.5. The weight ranges of titania, alumina, silica and water in the hydrosol expressed in terms of parts by weight H₂O, TiO₂ and Al₂O₃ per part by weight SiO₂ are as follows:

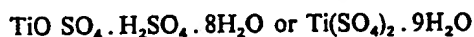
$H_2O=6$ to 25 parts per part SiO_2
 $TiO_2=0.01$ to 0.12 parts per part SiO_2
 $Al_2O_3=0.01$ to 0.15 parts per part SiO_2

5 When the hydrosol binder is converted to a dried gel product, it contains the following amount of SiO_2 , TiO_2 and Al_2O_3 expressed as percent by weight on a dry basis: 5

$SiO_2=78$ to 98
 $TiO_2=1$ to 10
 $Al_2O_3=1$ to 12

10 When the hydrosols of this invention are used to perpare zeolite/clay containing catalytic cracking catalysts, the hydrosol can be combined with the zeolite and if desired other weighting agents such as alumina, silica-alumina, and silica. The composite is suitably formulated to contain 15—35% by weight (dry basis) of hydrosol, 5—60% by weight zeolite and 5—60% by weight clay and other weighting agents. 10

15 The titanium salts used in the preparation of the hydrosols are soluble titanium salts, preferably soluble titanyl sulphate having the formula: 15



20 The aluminium salt is preferably an acid aluminium salt such as aluminium sulphate. The alkali metal silicate used in the preparation of the hydrosols is preferably sodium silicate which has a composition from 3.36 to 2.5 $SiO_2:Na_2O$ which may contain from about 5 to 20% by weight of the aforementioned sodium silicate dissolved in water. 20

25 The catalysts which may be prepared using the hydrosols of this invention may contain crystalline aluminosilicates such as type Y zeolite, or modified forms of type X and type Y zeolite which may be thermally treated and exchanged with rare earth ions as disclosed in United States 3,402,996, 3,607,043, or 3,676,368. Furthermore, the zeolite may be thermally stabilized as shown in United States 3,293,192 or 3,449,070. The catalysts in addition to zeolite may contain weighting agents such as clay which may be kaolin, metakaolin, or halloysite. Furthermore, the weighting agent may include inorganic oxides such as alumina, and silica-alumina. 25

30 The catalysts prepared from the hydrosol of this invention are particularly useful for the processing or converting of petroleum hydrocarbons. Typically, these catalytic cracking catalysts are used in fluid or fixed bed cracking processes wherein a hydrocarbon feedstock is contacted with the catalyst at a temperature of from about 700 to 1000°F. Furthermore our titania-alumina-silica hydrosol binders find application in the preparation of other hydrocarbon conversion catalysts such as hydro-cracking catalysts, isomerisation catalysts, and reforming catalysts as well as auto exhaust oxidation catalysts. The hydrosol binders may be combined with alumina to form extrudates, beads, and pills that may be used as supports for a variety of catalysts. Moreover the hydrosols may be spray dried to form hard attrition resistant composites of titania-alumina-silica possessing ion exchange capability. 30

35 A typical process which may be utilised to prepare the hydrosols in catalysts of the present invention is set forth in the drawing. As shown in the drawing, in a preferred method of operation to make a hydrosol according to this invention the source of titanium salt solution (which typically has a concentration of from about 1% to 10% by weight TiO_2 in water) is connected to a mixed salt tank. Also connected to the mixed salt tank is a source of aluminium salt solution (which can have a concentration of from about 1 to 8 $Al_2O_3\%$ by weight in water). The mixed salt tank is connected to a mixing pump. A source of alkali metal silicate solution is also connected to the mixing pump. The alkali metal silicate solution typically has a concentration of from about 5 to 20% by weight alkaline metal silicate in water. 35

40 The mixed titanium and aluminium salt solution, and alkaline metal silicate solution are metered to the mixing pump in amounts which provide the desired ratios of H_2O , TiO_2 , and Al_2O_3 to SiO_2 indicated above. The pH of the hydrosol is maintained at closely regulated levels of from about 2.5 to 3.5. In general it is found that the mixed titania aluminium salt solution will possess a pH of about 0.7 to 2.2 and the alkali metal silicate solution will have an initial pH of from about 11.3 to 40

45 50 55 60

12.0. In general it is preferred to maintain the hydrosol at a temperature of from about 60 to 75°F. prior to use. It is found that the hydrosol is relatively stable at these temperatures and may be held for a period of from about 1/4 to 1 hour prior to utilisation.

In the embodiment shown in the drawing the hydrosol is prepared in the mixing pump and then conducted to the mixer, preferably a high shear mixer. Also connected to the mixer are sources of clay slurry and zeolite slurry. The clay slurry will typically comprise kaolin slurried in water in amounts where from about 25 to 35% by weight kaolin is contained in the slurry. The zeolite slurry will typically contain from about 20 to 30 weight percent zeolite mixed in water. The pH of zeolite slurry may be adjusted to pH 3.8—4.5 with mineral acid. In the process shown in the drawing the clay and zeolite slurries are metered into the mixer along with a hydrosol feed stream from the mixing pump. The hydrosol, clay and zeolite are continuously mixed in the mixer and then fed to a spray drier wherein the hydrosol-clay-zeolite slurry is dried. Typically the spray drier is operated at an inlet gas temperature of from about 600 to 900°F. and the gas outlet temperature of from about 300 to 400°F. The spray dried catalyst product will be in the form of particles which typically possess a particle size range of from 20 to 300 microns. Subsequent to spray drying the catalyst composite is washed with water to remove soluble salts and may subsequently be exchanged with catalytically active or stabilizing ions such as rare earth.

The catalyst composites prepared in this way are found to possess a tough uniform homogeneous structure which is particularly attrition resistant. Furthermore, the catalyst composites will possess a surface area of from about 150 to 225 m²/g and a water pore volume of from about 0.20 to 0.30 cc/g. and a nitrogen pore volume of 0.08 to 0.15 cc/g.

Having described the basic aspects of the present invention the following examples are given to illustrate the specific embodiments thereof. In the examples the Davison Attrition Index (D.I.) was determined as follows:

A 7 g. sample is screened to remove particles in the 0 to 20 micron size range. The particles above 20 microns are then subjected to a 5 hour test in the standard Roller Particle Size Analyzer using a 0.07 inch jet and 1 inch I.D. U-Tube as supplied by American Instrument Company, Silver Spring, Maryland. An air flow of 21 litres per minute is used. The Davison Index is calculated as follows:

$$\text{Davison Index} = \frac{0-20 \text{ micron material formed during test}}{\text{Original } 20+\text{micron fraction}} \times 100$$

The catalysts were evaluated by comparing the activity of these catalysts with the activity of a standard catalyst containing rare earth faujasite. In this comparison both catalysts are subjected to the standard activity test described by Ciapetta and Henderson in the Oil and Gas Journal of October 16, 1967 at pages 88 to 93.

Example I

Using a system similar to that shown in the drawing 19.49 lbs. of mixed titanium sulphate-aluminium sulphate mixed salt solution containing as oxides 3.85 Wt. percent TiO₂ and 3.89 Wt. percent Al₂O₃ was continuously introduced to the mixing pump. Simultaneously, 80.51 lbs. of sodium silicate of 18°Be gravity and 3.36 SiO₂/Na₂O ratio was continuously introduced to the mixing pump. The two flowing streams reacted in the mixing pump and a hydrosol of 3.05 pH was continuously produced and collected.

One hundred pounds of hydrosol was transferred to a high speed mixer. While the hydrosol was being stirred, 32.6 lbs. of dry commercial KCS clay and 8.9 lbs. (dry basis) synthetic Na-Y faujasite as an aqueous slurry of 4.0 pH containing 33 percent solids were added. The composite mixed aqueous slurry of titania-alumina-silica hydrosol, KCS clay and synthetic-Na-Y faujasite was pumped to a commercial spray dryer having a rotating dispersing vane which rotated at 11,850 rpm and was dried at a dryer gas inlet temperature of 625°F. and a gas outlet temperature of 350°F. The spray dried material was washed with hot water to remove the sodium sulphate, exchanged with rare earth chloride solution, water washed and dried. The resulting catalyst had the properties set forth in the Table.

Example II

In a manner similar to Example I, 21.44 lbs of mixed titanium sulphate-

aluminium sulphate mixed salt solution containing as oxides 3.85 Wt.% TiO_2 and 3.89 Wt.% Al_2O_3 was continuously reacted with 78.56 lbs. of sodium silicate of 20°Be gravity and 3.36 $\text{SiO}_2/\text{Na}_2\text{O}$ ratio in the mixing pump to form a hydrosol of 3.05 pH.

One hundred lbs. of mixed hydrosol was transferred to a high speed mixer. While the hydrosol was being stirred, 35.6 lbs. of dry commercial KCS kaolin clay and 9.7 lbs. (dry basis) synthetic Na-Y faujasite as an aqueous slurry of 4.0 pH containing 35 Wt.% solids were added.

The composite mix of hydrosol, KSC clay and synthetic Y faujasite was pumped to a commercial spray drier and dried at a dryer gas inlet of 625°F and a gas outlet temperature of 350°F. The spray dried material was washed with hot water to remove the sodium sulphate, exchanged with rare earth chloride solution, water washed and dried.

The properties of the catalyst are set forth in the Table.

TABLE			
Example	I	II	
Total Volatiles % by Wt.	10.11	10.53	
Al_2O_3 , Wt. % (dry basis)	33.80	33.85	
Re_2O_3 , Wt. % (dry basis)	3.20	3.42	
Na_2O , Wt. % (dry basis)	0.55	0.39	
SO_4 , Wt. % (dry basis)	0.11	0.03	
TiO_2 , Wt. % (dry basis)	2.97	2.98	
Surface Area (m^2/g)	179	168	
Pore Volume (N)	0.12	0.11	
Pore Diameter	26	26	
Pore Volume (H_2O)	0.24	0.24	
D.I.	3	5	
J.I.	0.1	0.7	
Average Bulk Density (cc/g)	0.77	0.79	
Average Particle Size (microns)	60	78	
Microactivity after steaming at 1350°F.			
Sample, % conversion	81.2	81.5	
Standard, % conversion	75.0	75.0	
Binder			
Wt. % Al_2O_3	6.5	6.8	
Wt. % TiO_2	6.5	6.8	
Wt. % SiO_2	87.0	86.4	
Catalyst			
Wt. % Binder	24.8	24.0	
Wt. % Clay	58.8	57.6	
Wt. % Na-Y Zeolite	16.4	18.4	
After 1 Hour @ 1500°F Thermal Pretreatment of Sample			
D.I.	2	6	
J.I.	0.9	0.2	
Average Bulk Density (g/cc)	0.83	0.84	
Peak Height			
1000°F.	56	57	
1600°F.	50	51	
Microactivity @ 1350°F.			
Sample, % conversion	77.9	78.6	
Standard, % conversion	69.9	69.9	

It will be noted that the attrition order in these Examples is 3 and 5 respectively, whereas in Examples 1 and 2 of our Patent 4022714 the attrition order of the catalyst made from silica-titania hydrosol without alumina was 11 and 13 respectively.

Exempl III

A sample of spray dried hydrosol was prepared as follows:

23.0 lbs. of mixed titanium sulphate-aluminium sulphate solution containing as oxides 2.81 Wt. percent TiO_2 and 3.75 Wt. percent Al_2O_3 was continuously reacted with 83.15 lbs. of sodium silicate of 18°B gravity and 3.36 $\text{SiO}_2/\text{Na}_2\text{O}$ ratio in a mixing pump to form a hydrosol of 3.0 pH.

The 106.15 lbs. of mixed hydrosol was pumped to a commercial spray dryer and dried at a dryer gas inlet of 625°F. and a gas outlet temperature of 350°F. The spray dried material was washed with hot water to remove sodium sulphate and dried. The dried titania-alumina-silica compound had the following chemical analysis and physical properties:

TiO_2 Weight % (dry basis)=7.17% Bulk Density=0.58 g/cc
 Al_2O_3 Weight % (dry basis)=9.62% Surface Area=200 m^2/g
 SiO_2 Weight % (dry basis)=82.15% P.V.(H_2O)=0.22 cc/g
 Na_2O Weight % (dry basis)=0.31% P.V.(N_2)=0.11 cc/g
 SO_4 Weight % (dry basis)=0.75%

Example IV

In a manner similar to Example III, 68.3 lbs. of mixed titanium sulphate-aluminium sulphate solutions containing as oxides 1.29 Wt. percent TiO_2 and 1.32 Wt. percent Al_2O_3 was continuously reacted with 74 lbs. of sodium silicate of 16.5°Be gravity and 3.36 $\text{SiO}_2/\text{Na}_2\text{O}$ ratio in the mixing pump to form a hydrosol of 3.15 pH.

The 142.3 pounds of mixed hydrosol was pumped to a commercial spray dryer and dried at a dryer gas inlet of 600°F. and a gas outlet temperature of 350°F. The spray dried material was washed with hot water to remove sodium sulphate, exchanged with rare earth chloride solution, water washed and dried.

The product had a surface area of 220 m^2/g , contained 5.84 Wt. percent (D.B.) Re_2O_3 and had a catalytic activity of 14.4 percent conversion compared to a standard catalyst activity of 71.4 percent conversion.

This behaviour indicates the dried matrix possesses some catalytic activity as well as cation exchangeability.

WHAT WE CLAIM IS:—

1. A hydrosol suitable for preparation of a hydrocarbon-cracking catalyst which comprises components yielding titania-alumina and silica in the following amounts by weight TiO_2 , Al_2O_3 , SiO_2 and H_2O :

- (a) 0.01 to 0.12 parts TiO_2 per part SiO_2 ,
- (b) 0.01 to 0.15 parts Al_2O_3 per part SiO_2 , and
- (c) 6 to 25 parts H_2O per part SiO_2 , said hydrosol having a pH of from 2.5 to 3.5.

2. The hydrosol of claim 1 wherein said TiO_2 is derived from soluble titanium sulphate and said Al_2O_3 is derived from aluminium sulphate.

3. The hydrosol of claim 1 or 2 which is obtained by combining an aqueous solution of a titanium salt and an aluminium salt with a solution of alkali metal silicate.

4. The hydrosol of claim 3 wherein said alkali metal silicate is sodium silicate.

5. A particulate titania-alumina-silica sol obtained by drying a hydrosol as claimed in any of claims 1 to 4.

6. A process for preparing a hydrocarbon conversion catalyst which comprises:

- (a) preparing an aqueous slurry of a crystalline aluminosilicate zeolite and a titania-alumina-silica hydrosol binder, and
- (b) spray drying said slurry to form discrete catalyst particles.

7. A process according to claim 6 in which there is used a hydrosol according to claim 2.

8. A process according to claim 7 in which there is used a hydrosol having a pH of 2.8 to 3.2.

9. The process of claim 8 wherein said slurry has a pH of about 3.0 to 3.9 prior to drying.

10. The process of any one of claims 6 to 9 wherein the slurry is maintained at a temperature of $21 \pm 3^\circ\text{C}$ prior to drying.

11. The process of any of claims 6 to 10 wherein said slurry is spray dried to obtain a catalyst having a particle size of from 20 to 300 microns.

12. The process of any of claims 6 to 11 wherein said catalyst is washed to remove soluble impurities.

13. The process of any of claims 6 to 12 wherein said catalyst is exchanged with a solution of rare earth cations.

5 14. The process of any of claims 6 to 13 wherein said zeolite is a type Y zeolite having a silica to alumina ratio of 3.5 to 5.5. 5

10 15. The process of any of claims 6 to 14 wherein there is formed a catalyst which contains from 5 to 60% by weight zeolite, from 0 to 80% by weight clay, from 15 to 35% by weight hydrosol binder, and from 0 to 30% by weight additional alumina. 10

16. A hydrocarbon conversion catalyst when prepared by a process as claimed in any of claims 6 to 15.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1981
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of
the Original on a reduced scale

